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Conference paper for the American Chemical Society National Conference, San Diego, California in 25-29 March 2012.

14. ABSTRACT

Incompletely-condensed fluoroalkyl-functional Polyhedral Oligomeric SilSesquioxanes (F-POSS) have been synthesized *via* a scaleable three-step synthetic process with an overall yield of 52%. The primary byproduct of each step in the synthesis is the completely-condensed F-POSS starting material, which enables the recycling of the starting materials. The incompletely condensed structures were readily reacted with a variety of functional dichlorosilanes to introduce reactive or unreactive functionality and produce unsymmetrical F-POSS structures. Chemical structures were confirmed by elemental analysis, multinuclear NMR (^{1}H, ^{13}C, ^{19}F, and ^{29}Si), and FT-IR methods. Single crystal X-ray diffraction was used to elucidate the crystal structure of the precursor F-POSS disilanol. The functionalized F-POSS structures were found to possess variable solubility properties, generally superior to those of the closed-cage F-POSS starting material. Dynamic contact angle measurements of these compounds were examined using water and hexadecane as the wetting liquids. Copolymers of poly(methyl methacrylate) containing F-POSS were synthesized from methacrylate F-POSS macromers. These novel structures can be used as building blocks for the development of low surface energy materials.

15. SUBJECT TERMS

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FUNCTIONALIZED FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (F-POSS)

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Propulsion Directorate

Edwards Air Force Base, CA

San Diego, CA *ACS Meeting 2012*

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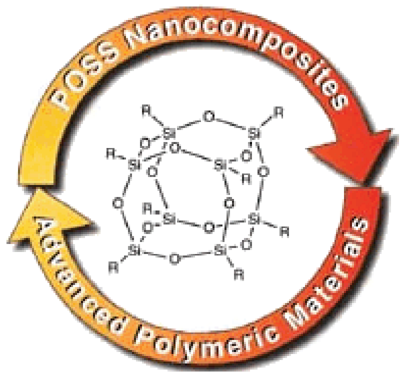
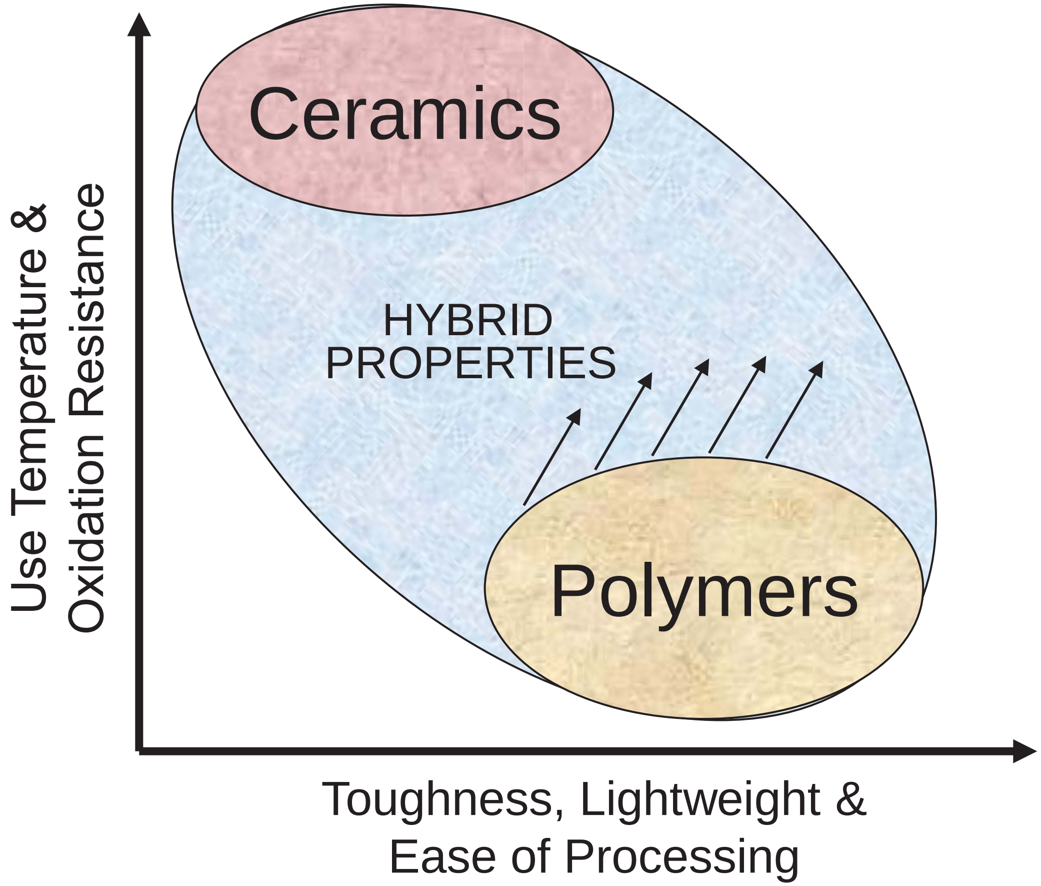


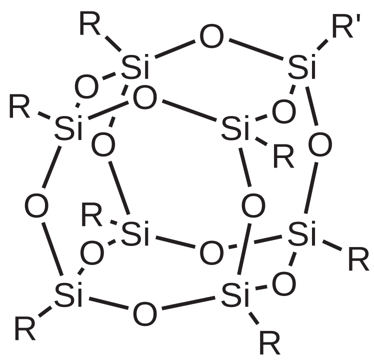
Financial Support:

Air Force Office of Scientific Research

Air Force Research Laboratory, Propulsion Directorate

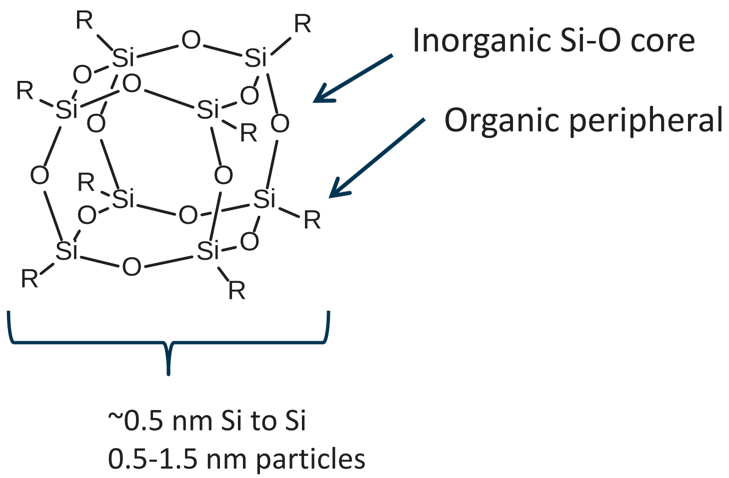
Hybrid Inorganic/Organic Polymers





POSS $(RSiO_{1.5})_n$

- Organic-inorganic framework
- Well-defined, 3-D nanostructure
- Can carry functional groups
- Thermally and chemically robust
- Used in thermoset and thermoplastic polymers, temperature nanocomposites, coatings, surface modifiers, and many other applications



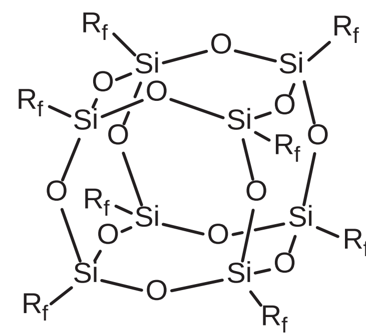
Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* ***2010****, 110, 2081.*

Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Current Opinion in Solid State and Materials Science* ***2004****, 8, 21.*

Introduction F-POSS

- Fluorinated polyhedral oligomeric silsesquioxane (F-POSS) possesses one of the lowest surface energies leading to the creation of superhydrophobic and oleophobic surfaces
- Close-caged structures are accessible and have proven versatile in polymer composites
  - Limitations
    - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
  - Open door for use a *building block* material for *low surface energy materials*
- Applications
  - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
    - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
  - Effects on polymer composite properties
    - Wetting, phase behavior, solubility, etc….

PMMA + 44 wt% POSS electrospun coating (beads on a string) morphology (water, methanol, diiodomethane, octane)



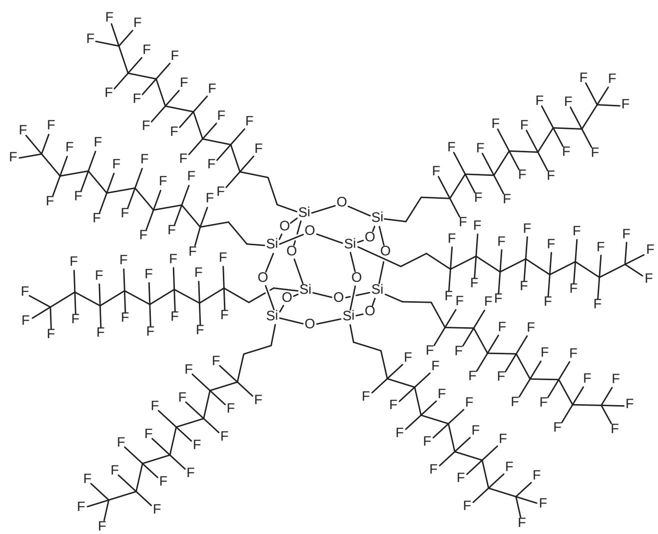
Fluorodecyl POSS
$R_f = CH_2CH_2(CF_2)_7CF_3$

(a) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D., *Angew. Chem., Int. Ed.* **2008,** *47*, 4137-4140; (b) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W., Jr., *Macromolecules* **2007,** *40*, 9517-9522; (c) Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M., *Chem. Commun.* **2007**, 4992-4994. (d) Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H., *Adv. Mater.* **2009,** *21*, 2190-2195; (e) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinely, G. H.; Cohen, R. E., *Proc. Natl. Acad. Sci. U. S. A.* **2008,** *105*, 18200-18205,; (c) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E., *Science* **2007,** *318*, 1618-1622; (f) Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., *ACS Appl. Mater. Interfaces* **2010,** *2*, 3544-3554.

Fluorinated polyhedral oligomeric silsesquioxane (F-POSS)

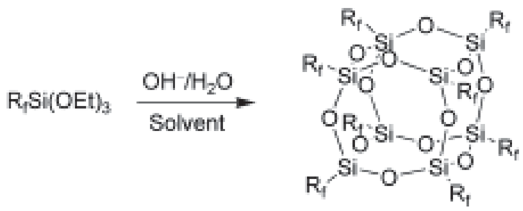
F-POSS, a subclass of POSS which consists of a silicon-oxide core [$SiO_{1.5}$] with a periphery of long-chain fluorinated alkyl groups.

F-POSS possesses one of the lowest surface energies leading to the creation of superhydrophobic and oleophobic surfaces.

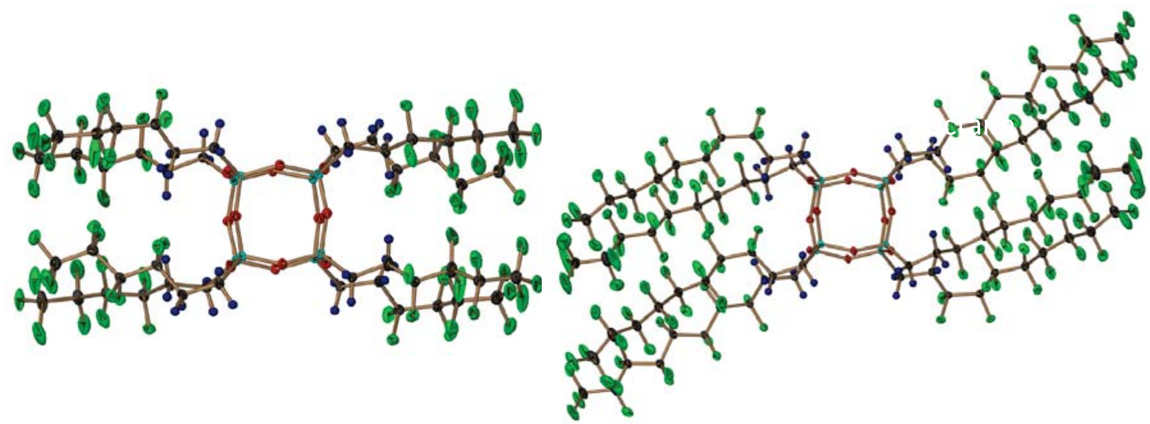


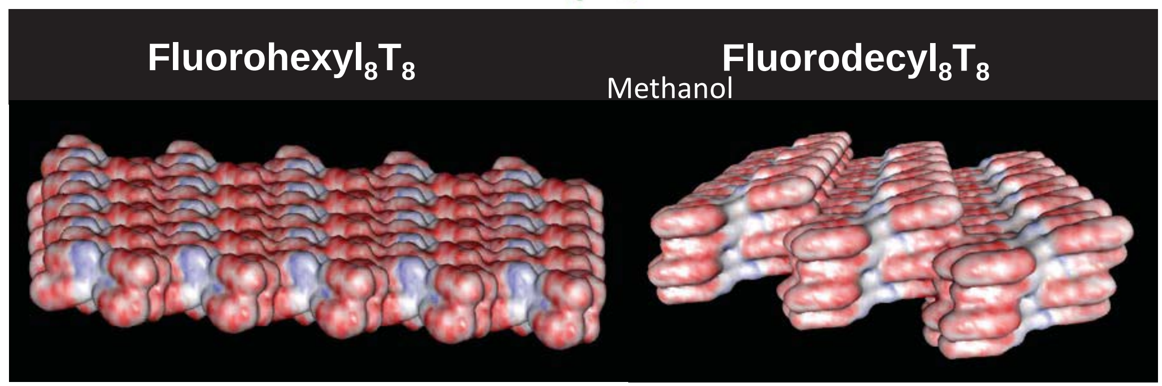
(a) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D., *Angew. Chem., Int. Ed.* **2008,** *47*, 4137-4140; (b) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W., Jr., *Macromolecules* **2007,** *40*, 9517-9522; (c) Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M., *Chem. Commun.* **2007**, 4992-4994. (d) Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H., *Adv. Mater.* **2009,** *21*, 2190-2195; (e) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinely, G. H.; Cohen, R. E., *Proc. Natl. Acad. Sci. U. S. A.* **2008,** *105*, 18200-18205,; (c) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E., *Science* **2007,** *318*, 1618-1622; (f) Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., *ACS Appl. Mater. Interfaces* **2010,** *2*, 3544-3554.

Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS)



FH R_f = $CH_2CH_2CF_2CF_2CF_2CF_3$
FO $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$
FD $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$





Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D. *Angew. Chem., Int. Ed.* ***2008,*** *47, 4137.* (left)
Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. *Science* ***2007****, 318, 1618.* (right)

Functional F-POSS

- Close-caged structures are accessible and have proven versatile in polymer composites
  - Limitations
    - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
  - Open door for use a *building block* material for *low surface energy materials*
- Applications
  - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
    - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
  - Effects on polymer composite properties
    - Wetting, phase behavior, solubility, etc….

Methods to Produce Incompletely Condensed Silsesquioxanes

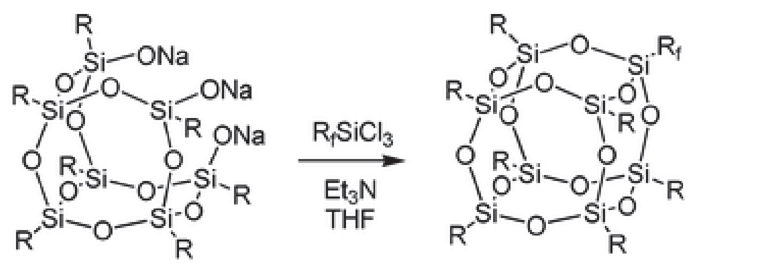
- Bottom-up approach
  - Acid or base mediated from $RSiCl_3$ or $RSi(OR)_3$
  - Condensation reaction
  - Balance of stoichiometry, temperature, reaction time, patience, and luck
  - Stopping POSS synthesis early, before cage fully condenses
  - More common approach
- Top-down Approach
  - Strong acid or base mediated
  - Starting from a POSS cage
  - Conversion of Si-O-Si bonds to Si-O $^{(-)}$ C$^{(+)}$ or Si-OH bonds
  - Opening up POSS cage

Which method can be applied to F-POSS?

Feher, F. J.; Terroba, R.; Ziller, J. W. *Chemical Communications* ***1999***, 2309. Feher, F. J.; Newman D.A;. Walzer, J.M., *J. Am. Chem. Soc.,* **1989**, 111, 1741. Feher, F. J.; Soulivong, D.; Nguyen, F.; Ziller, J. W. *Angew.Chem. Inter. Ed.**1998**, 37,* 2663. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* ***1998,*** 1279.

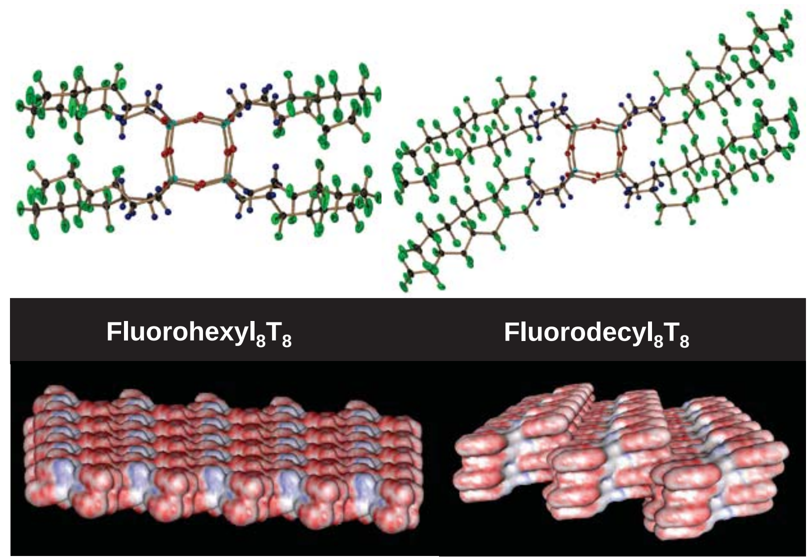
Trifluoropropyl Example

- Small chain F-POSS (propyl) have been developed and studied
- Demonstrate the robustness of an incompletely condensed silsesquioxane to functionalization



1 R = $CH_2CH_2CF_3$

2 R_f = $CH_2CH_2CF_3$
3 $CH_2CH_2(CF_2)_5CF_3$
4 $CH_2CH_2(CF_2)_7CF_3$
5 $CH_2CH_2(CF_2)_9CF_3$
6 $CH_2CH_2CH(CF_3)_2$
7 $CH_2CH_2CH_2OCF(CF_3)_2$
8 CH_3
9 $CH_2CH_2C_6H_5$



Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M. *Chem. Commun.* ***2007**, 4992.* Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D. *Angew. Chem., Int. Ed.* ***2008**, 47, 4137.*

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  - Balance of stoichiometry, temperature, reaction time, patience, and luck
  - Stopping POSS synthesis early, before cages closes
  - More common approach

- Top-down Approach
  - Strong acid or base mediated
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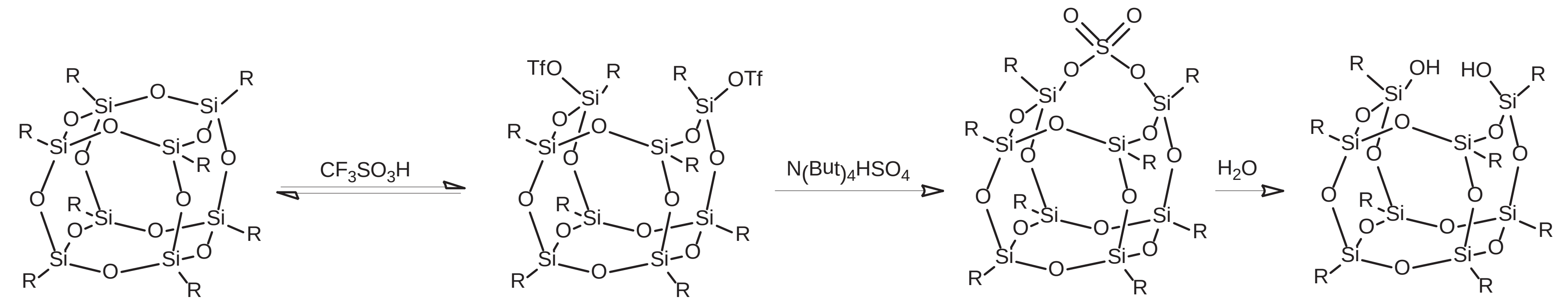
Incompletely Condensed Silsesquioxane

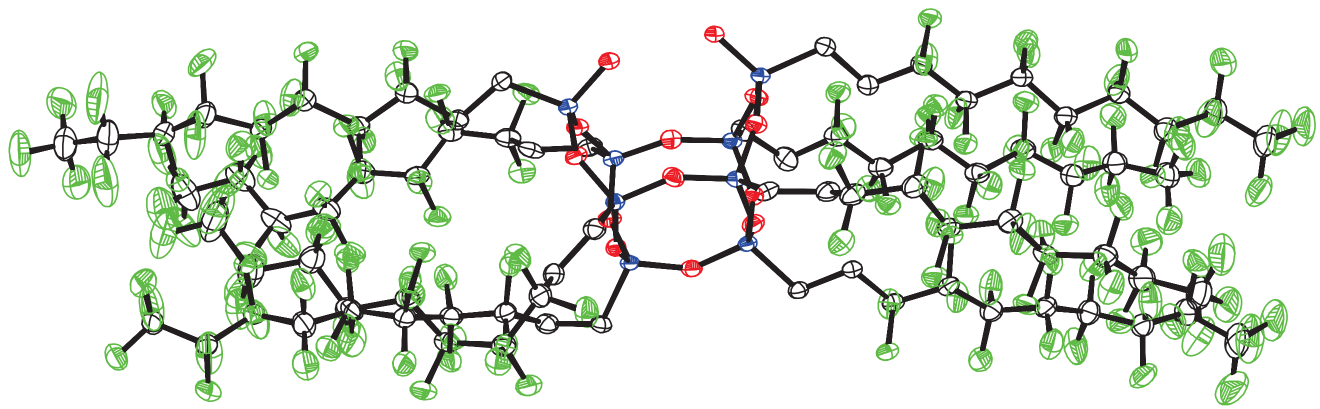


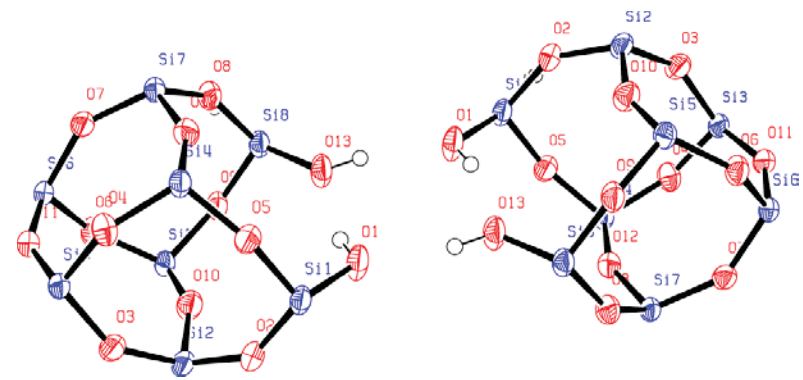
$R_f = CH_2CH_2(CF_2)_7CF_3$

- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.*

Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, **2011**, *133*, 20084.

X-Ray Crystal Structure of Disilanol

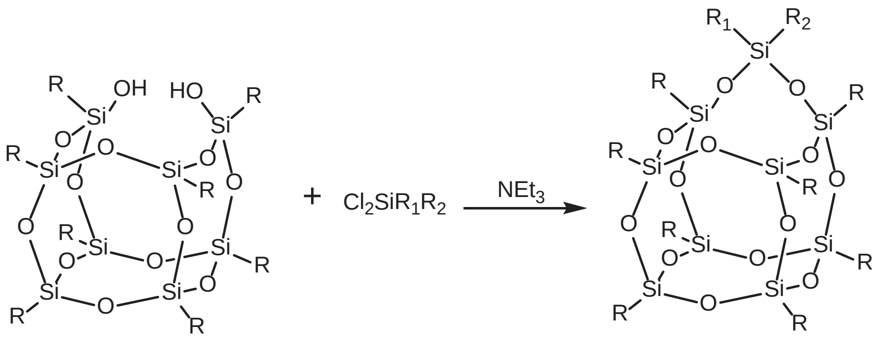




- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- M_r=,monoclinic, space group P2(1)/c , a=11.84(10) Å, b=57.11(6) Å, c=19.06(2) Å, α= 90.00°, β=92.21(10) °, γ=90.00 °, V= 12878(2) Å^3

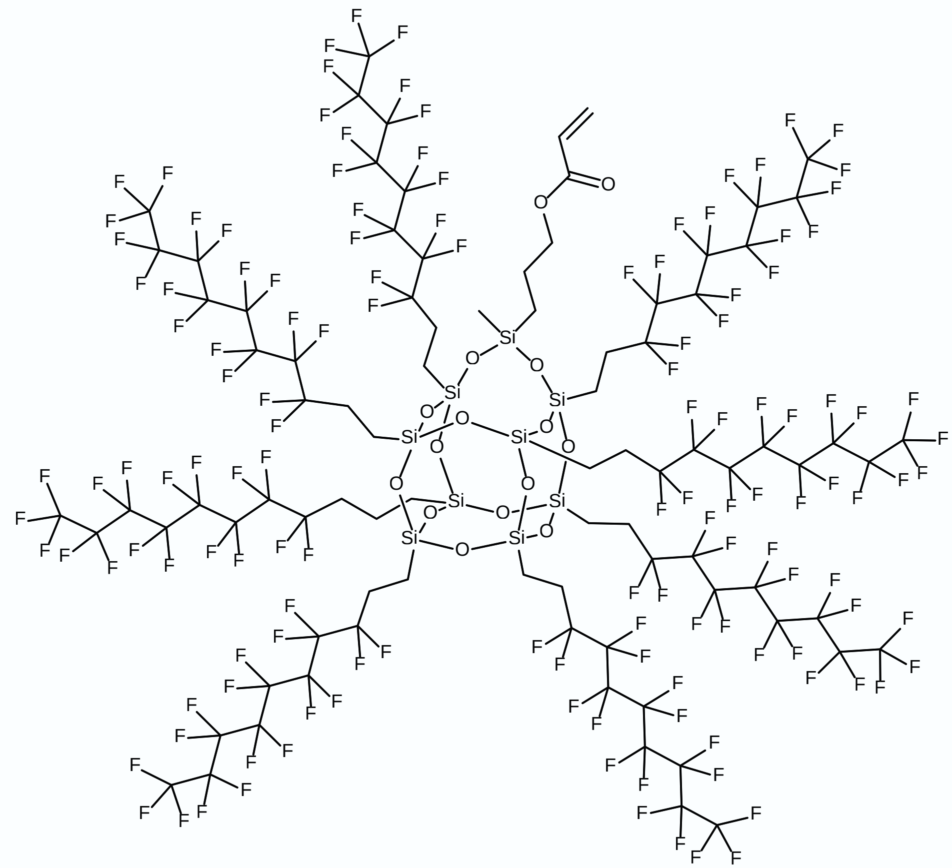
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, **2011**, *133*, 20084.

Edge Capping Reactions



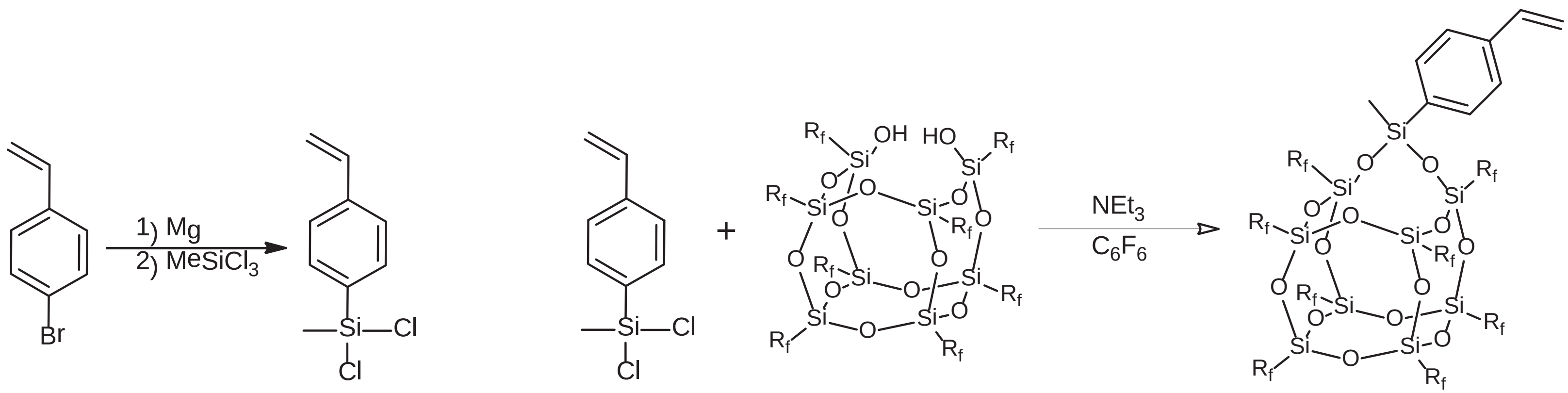
R = $CH_2CH_2(CF_2)_7CF_3$
R_1 = CH_3
R_2 = $CH_2CH_2CH_2$ OC(O)CHCH$_2$

- Edge capping reactions typically have 40-70% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes

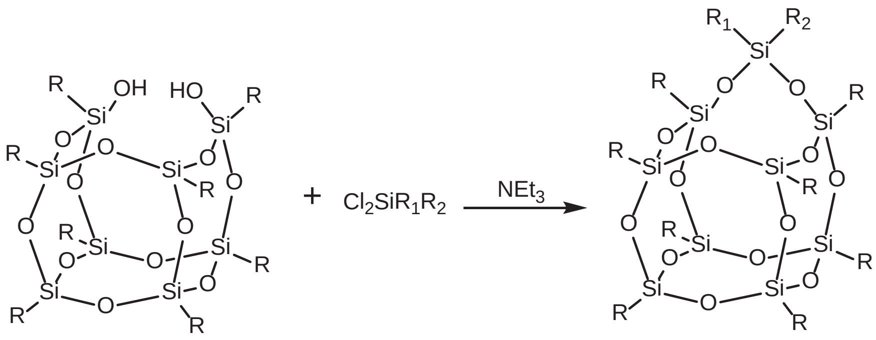


Macromer/RBM = 4178 g/mol

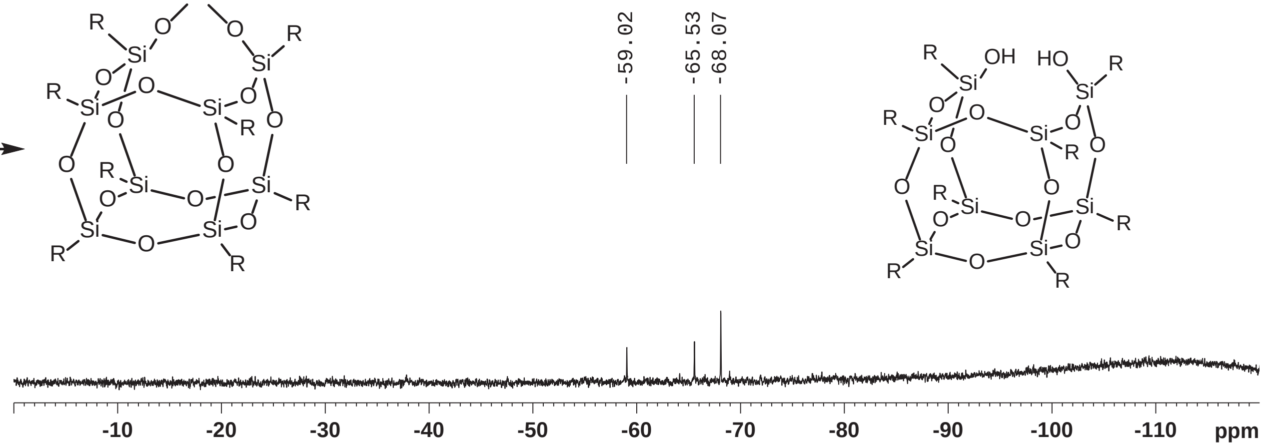
Styrene Monomer Synthesis

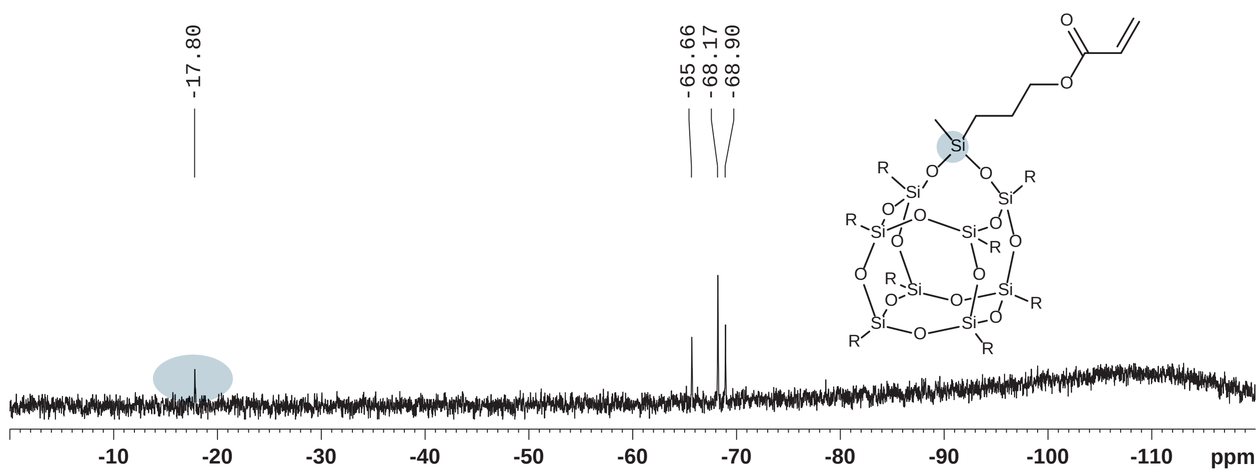


Edge Capping Reactions



R = $CH_2CH_2(CF_2)_7CF_3$
R_1 = CH_3
R_2 = $CH_2CH_2CH_2$ OC(O)CHCH$_2$



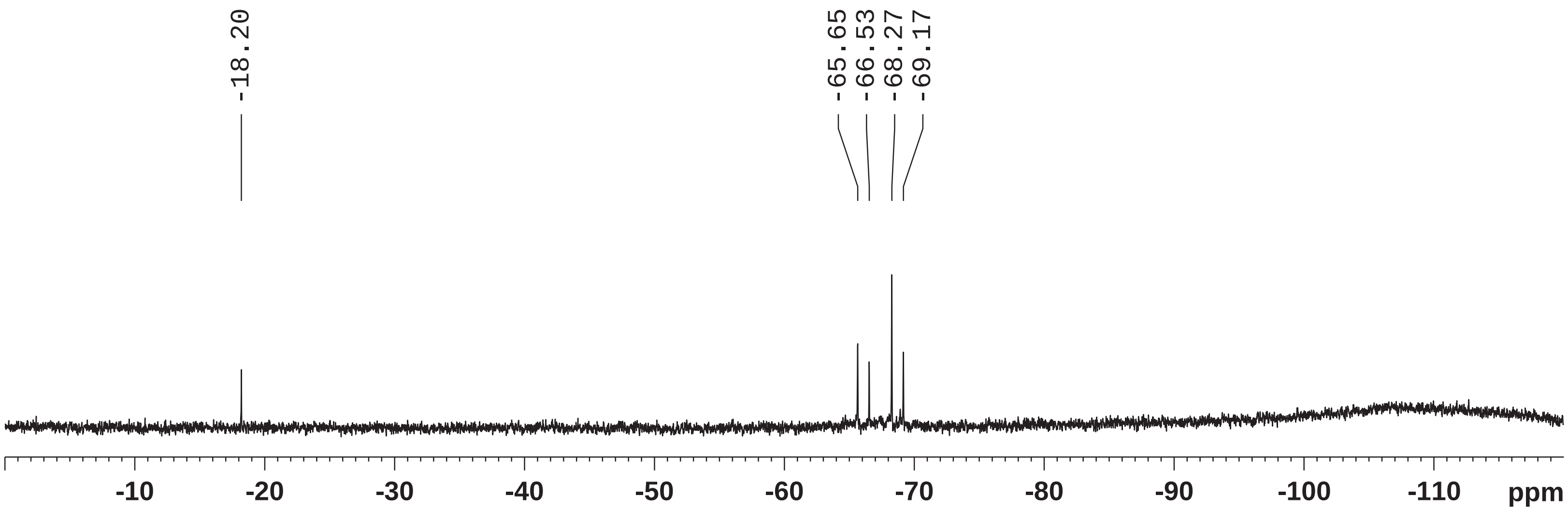


^{29}Si NMR taken in fluorinated solvent

- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**

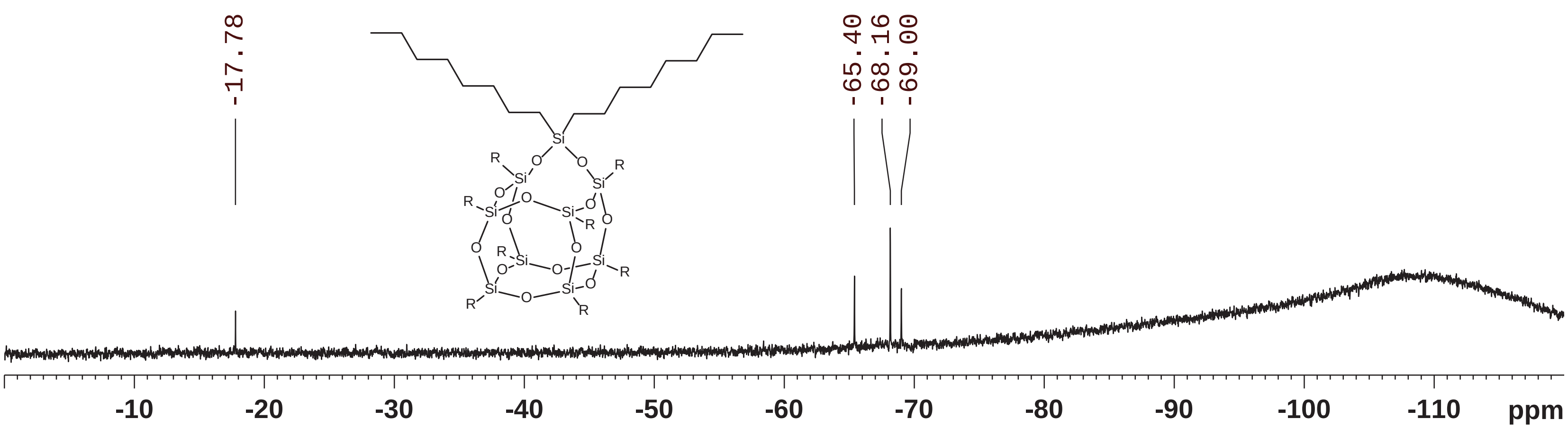
Separation of T_8 from Product

Before



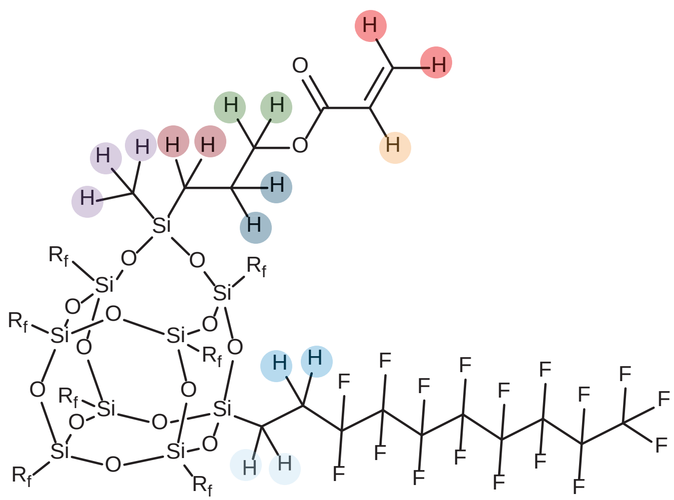
^{29}Si NMR taken in fluorinated solvent

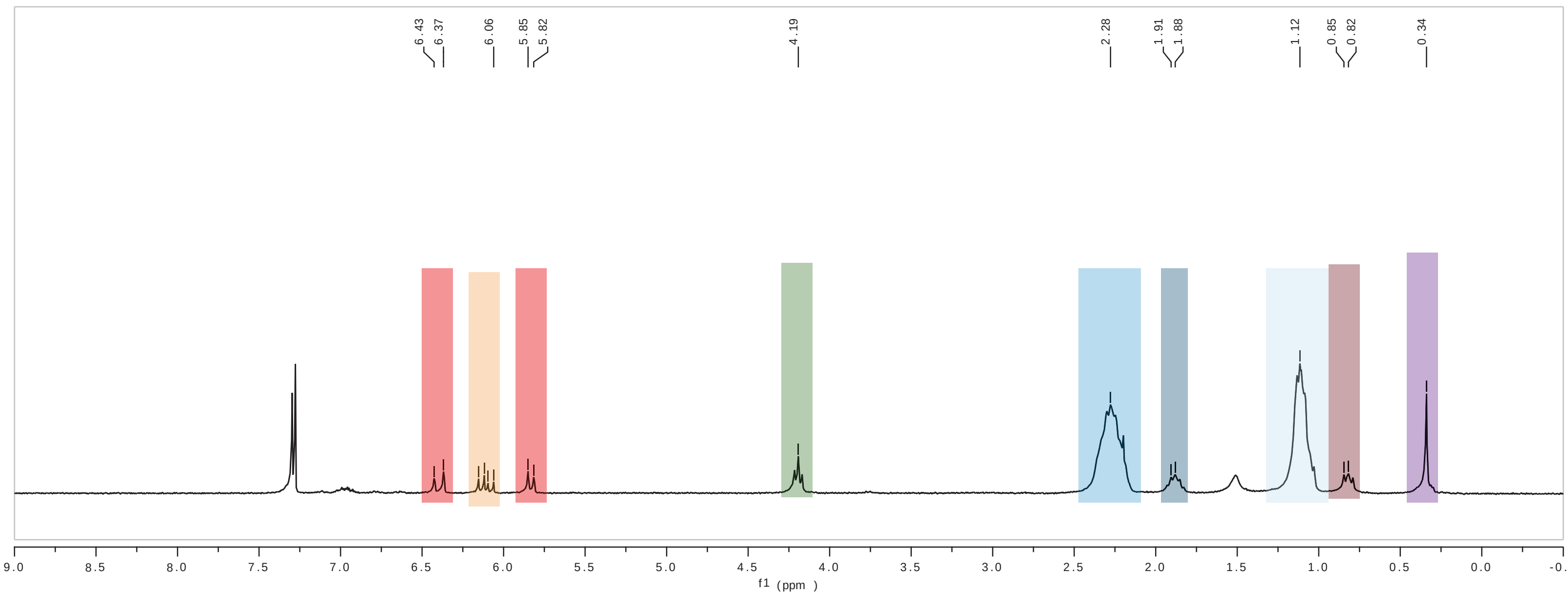
After



^{29}Si NMR taken in **diethyl ether-d_{10}**

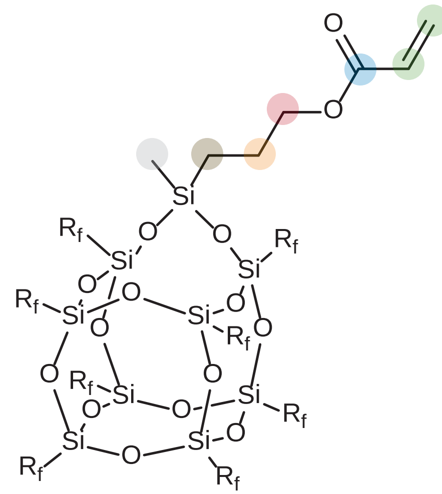
^{1}H NMR Characterization of Compounds

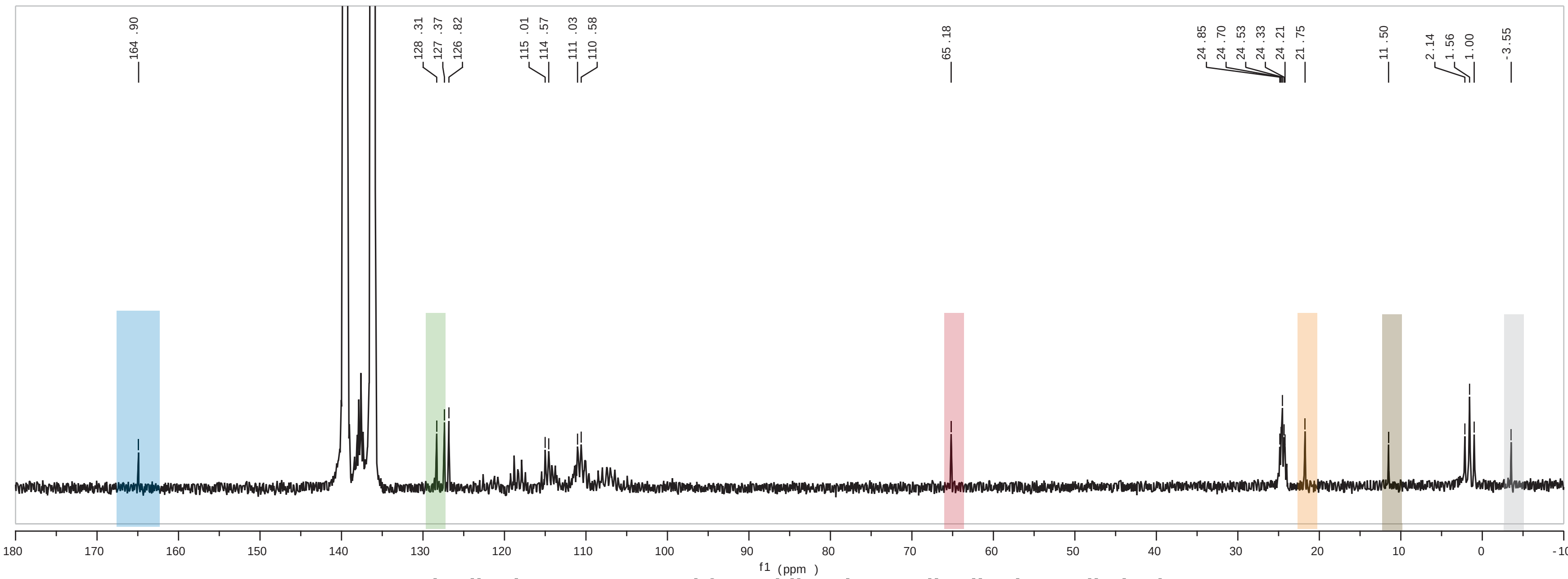




^{19}F NMR taken in diethyl ether. ^{1}H NMR taken in $C_6F_6/CDCl_3$ mixture.

^{13}C NMR Characterization of Compounds





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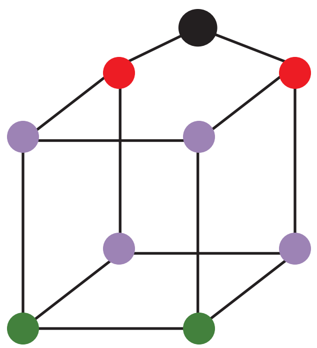
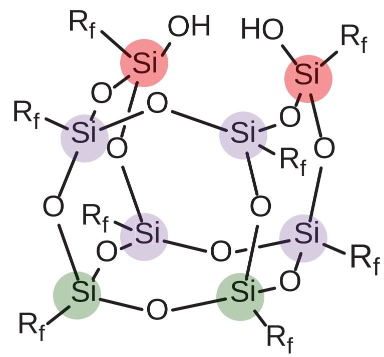
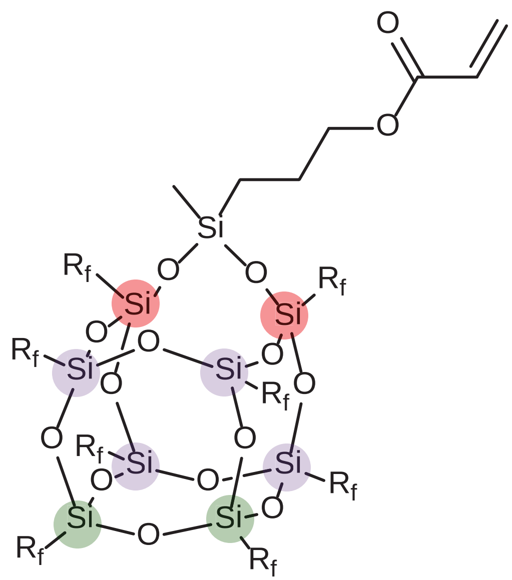
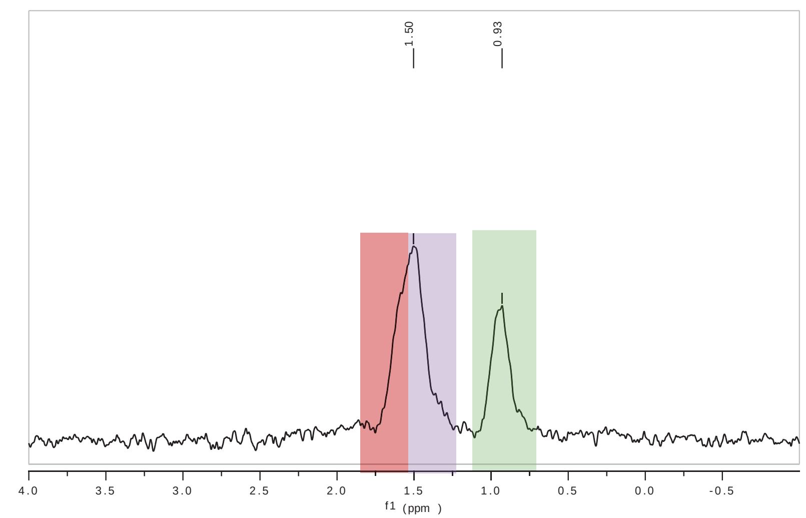
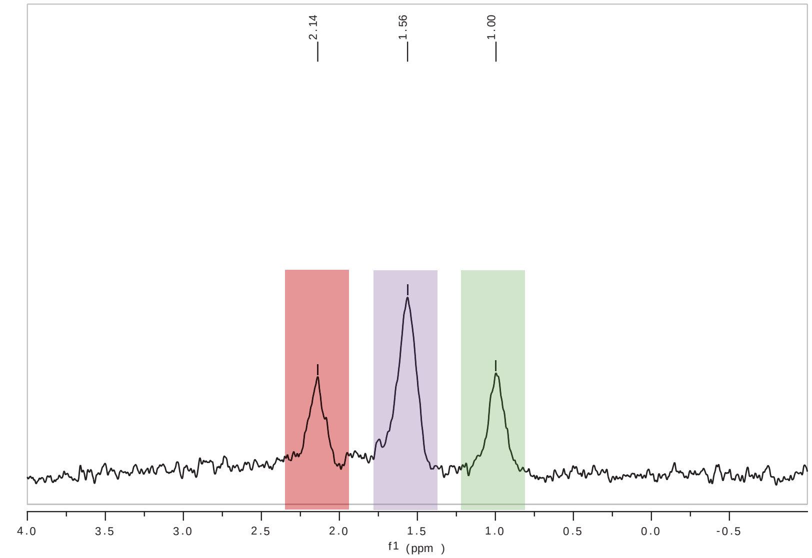
^{13}C NMR Characterization of Compounds



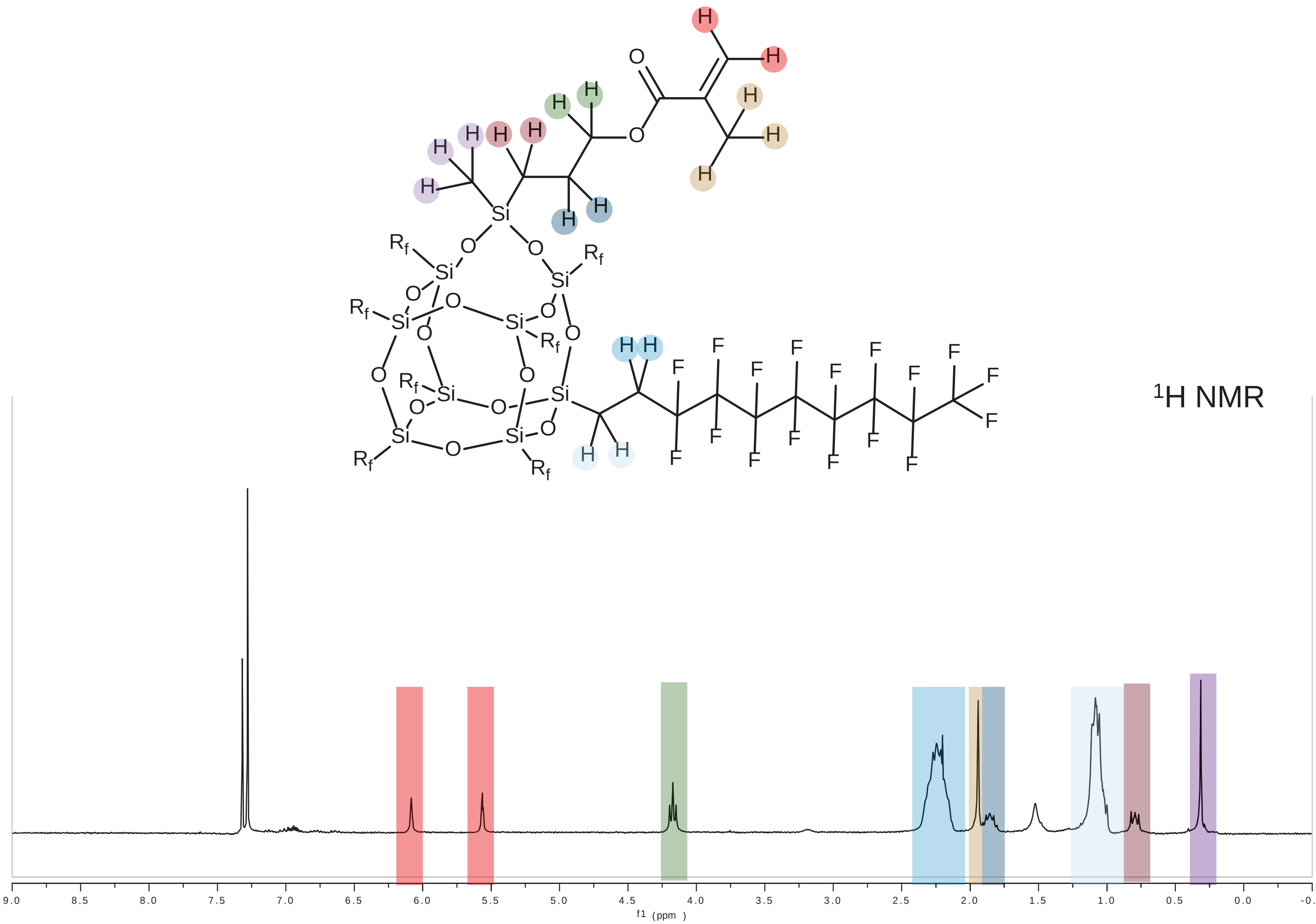






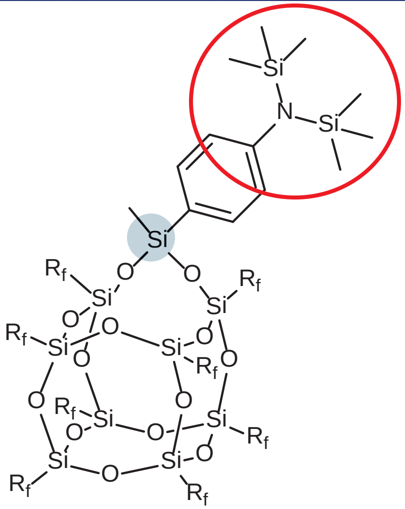


^{1}H NMR Characterization of Compounds

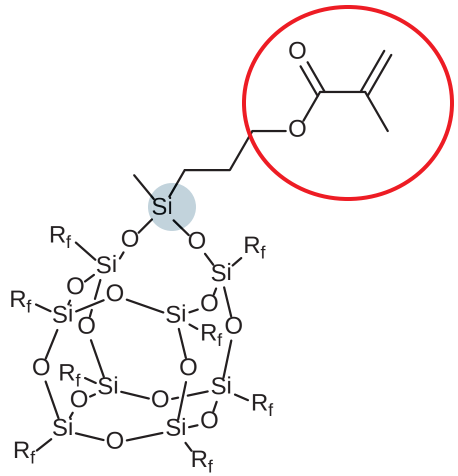


^{19}F NMR taken in diethyl ether. ^{1}H NMR taken in $C_6F_6/CDCl_3$ mixture.

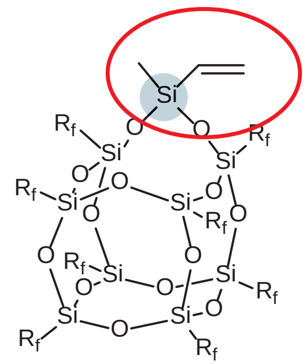
F-POSS Structures Synthesized



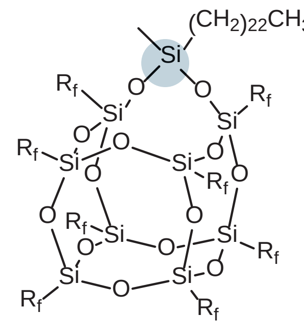
-29.5 ppm



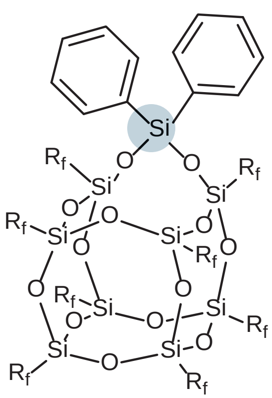
-17.8ppm



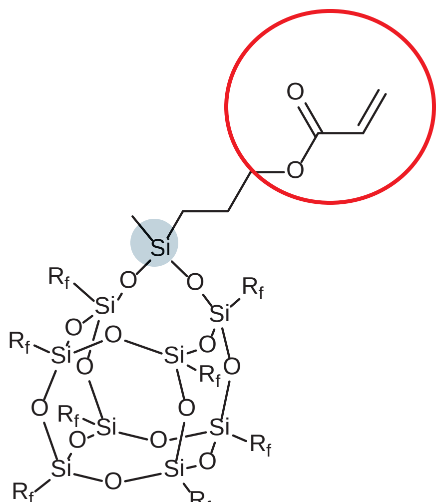
-32.1 ppm



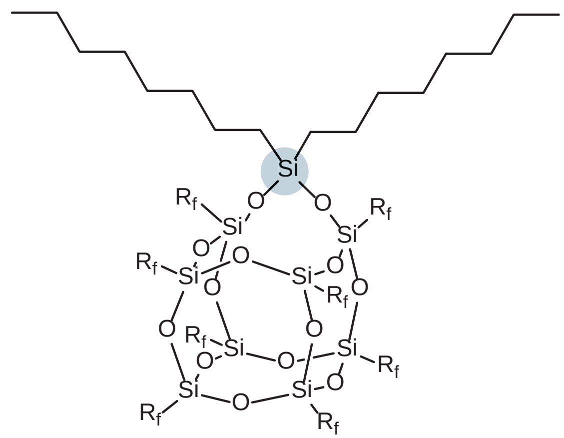
-17.8 ppm



-45.5 ppm



-17.1 ppm

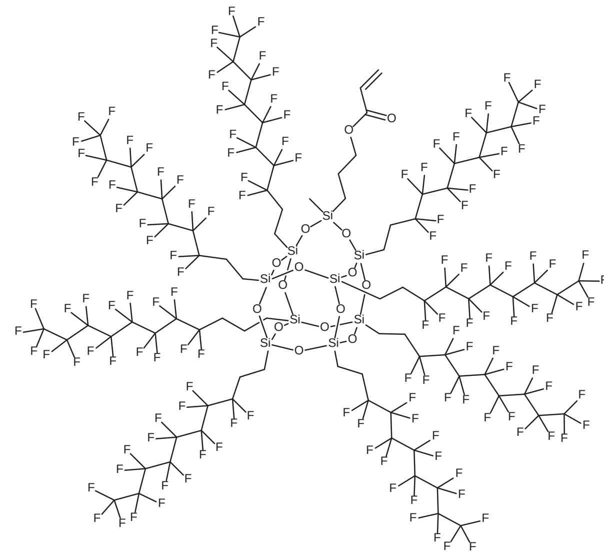


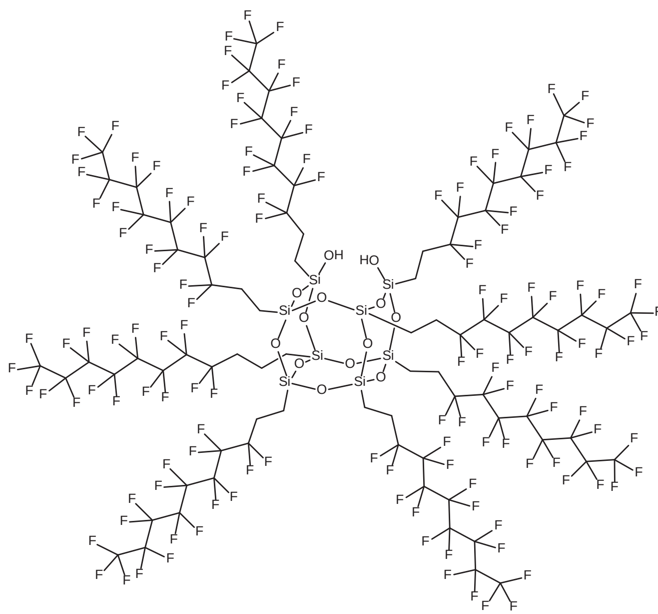
-17.9 ppm

R = $CH_2CH_2(CF_2)_7CF_3$

Contact Angle Measurements

- Non-wetting surfaces can be developed by a combination of three parameters
  - Chemical functionality (high fluorine content)
  - Roughness (micro- and nanoscale)
  - Surface Geometry (re-entrant curvature)
- *What type of influence will functional groups have on F-POSS surface properties?*
- *Solvent impact?*





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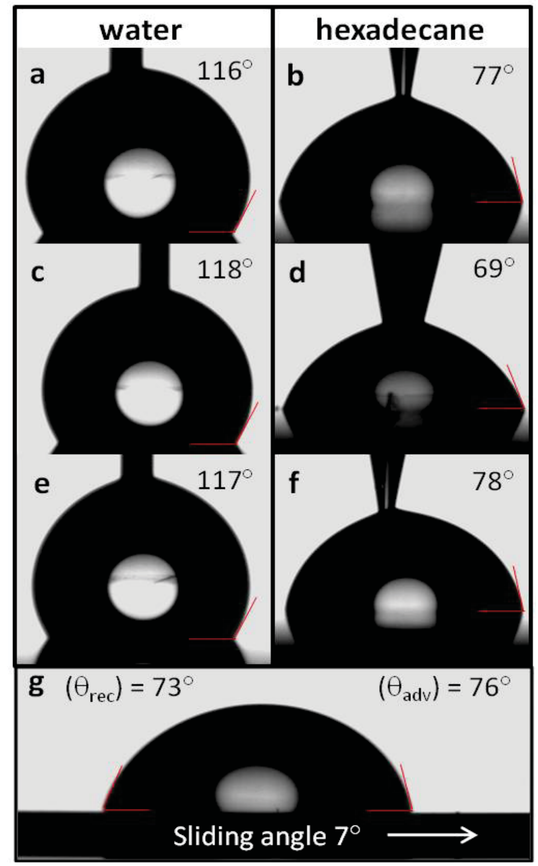
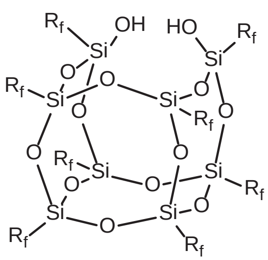
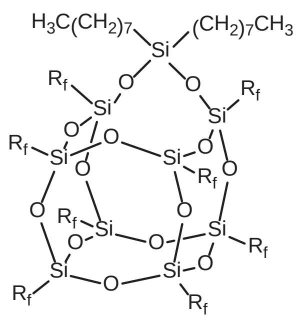
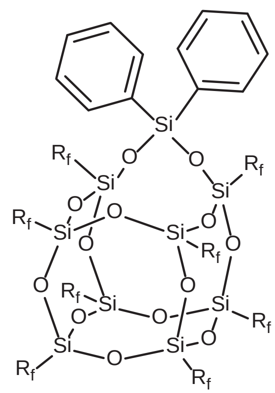


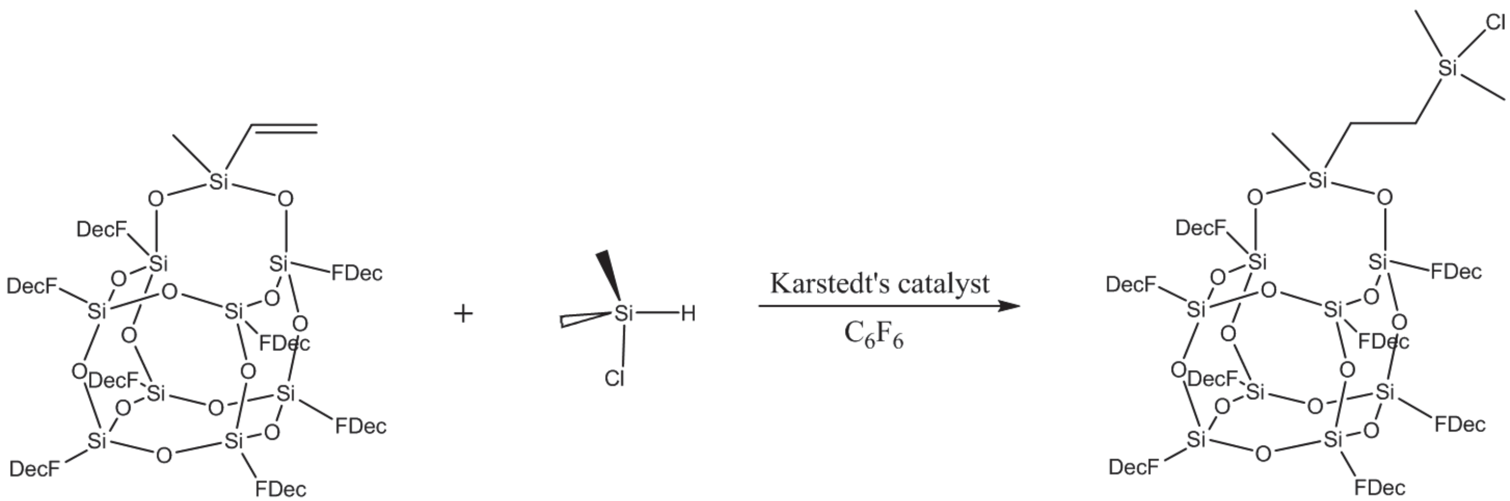
Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10 μL) rolling off surface coated with compound **diphenyl** (g).







F-POSS Silane Coupling Reaction

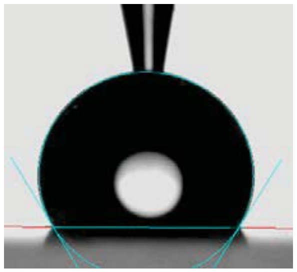


• Chlorosilyl-functional fluoroPOSS compound synthesized from the Pt(II) catalyzed hydrosilyation of vinyl-functional fluoroPOSS and dimethylchlorosilane

• Desired compound successfully synthesized in high yield

•Characterized by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR

Dynamic Contact Angle Measurements

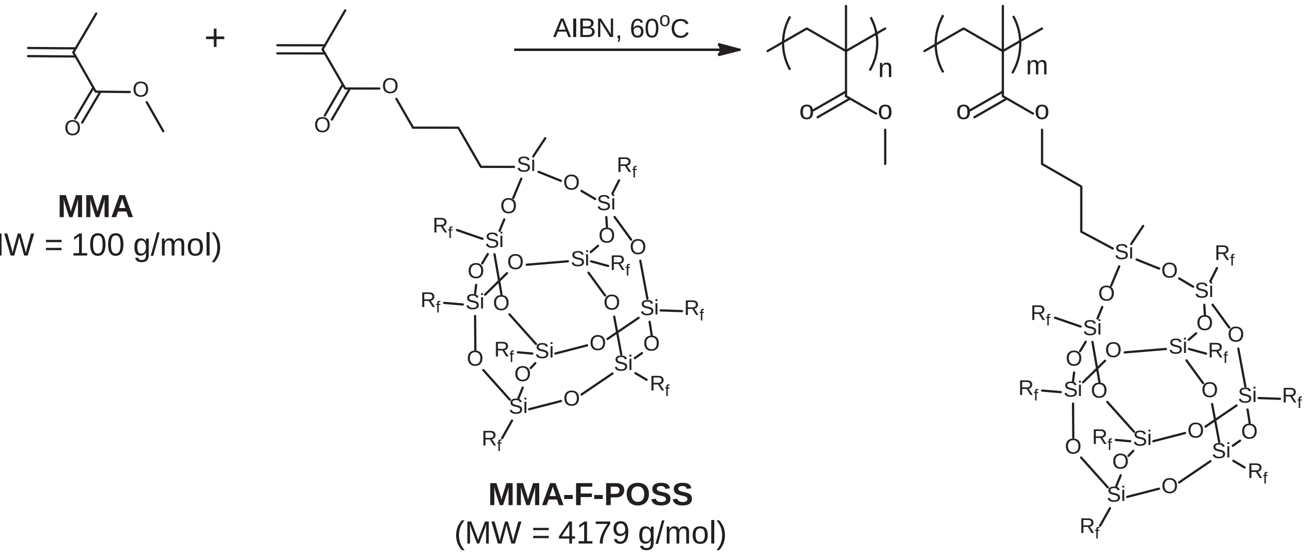


Functional Group on F-POSS	water		hexadecane	
	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
F-POSS*	124 ± 0.5°	109.6 ± 0.7°	79.1 ± 0.4°	65.1 ± 0.5°
Si-$(OH)_2$	116.8 ± 0.4°	111 ± 0.6°	77.4 ± 0.4°	74.4 ± 0.8°
Si-$(CH_3)(CH{=}CH_2)$	116.2 ± 0.4°	100.6 ± 0.8°	78.4 ± 0.3°	70.6 ± 2.3°
Si$((CH_3)((CH_2)_3OC(O)CCH{=}CH_2)$	118.2 ± 1.0°	90.6 ± 1.0°	76.8 ± 0.3°	64.8 ± 1.0°
Si-$(CH_3)(\ (CH_2)_3OC(O)C(CH_3){=}CH_2)$	117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°
Si-$(CH_3)((CH_2)_{22}CH_3)$	117.9 ± 0.4°	96.9 ± 1.9°	78.0 ± 0.4°	16.2 ± 5.5°
Si-$(C_6H_5)_2$	116.2 ± 0.4°	110.5 ± 0.5°	76.0 ± 0.8°	73.2 ± 0.4°
Si-$((CH_2)_7CH_3)_2$	117.9 ± 0.5°	95.5 ± 0.4°	69.1 ± 1.2°	23.1 ± 1.2°

Samples (10 mg/mL) were spin casted on oxygen-plasma cleaned Si wafers at 900 rpm for 30 seconds. Contact angle measurements were run in triplicate. Surface roughness < 5nm (AFM and Optical Profilometry).

*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3544.

Initial Copolymerizations



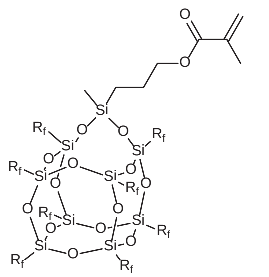
MMA
(MW = 100 g/mol)

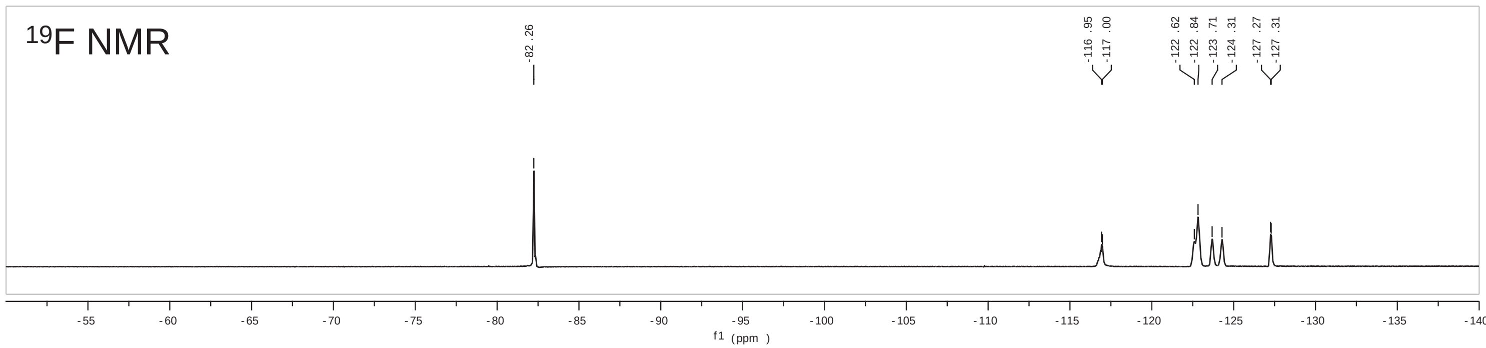
MMA-F-POSS
(MW = 4179 g/mol)

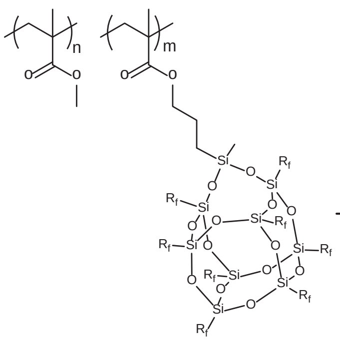
Sample #	Weight (g) MMA-F-POSS	MMA	Weight (%)F-POSS	Monomer (mmol) MMA-F-POSS	MMA	Mol Ratio (MMA:MMA-F-POSS)	Initiator (mol %)	Conversion (%)	Weight (%) FPOSS*
1	0.085	1.31	6.3	0.02	13.1	655	0.5	42	2.74
2	0.362	1.31	21.6	0.09	13.1	145	0.2	71	14.4
3	0.50	3.50	12.5	0.12	35.0	291	1		
4	1.00	3.00	25.0	0.24	30.0	125	1	62.5	
5	2.00	2.00	50.0	0.47	20.0	42	0.2	92.5	

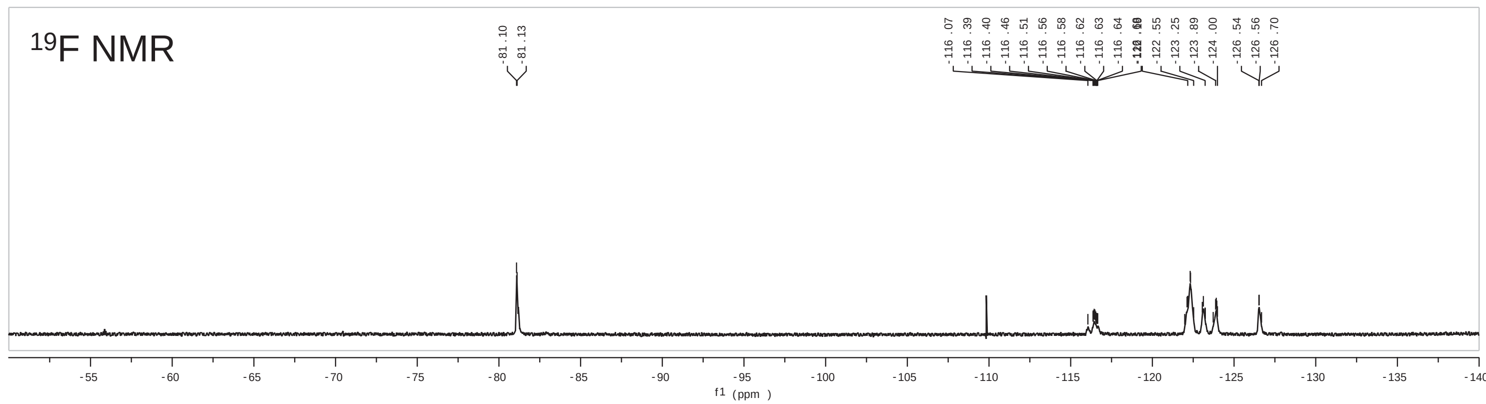
*Weight (%) of F-POSS was calculated from elemental analysis of Fluorine content in the final polymer.

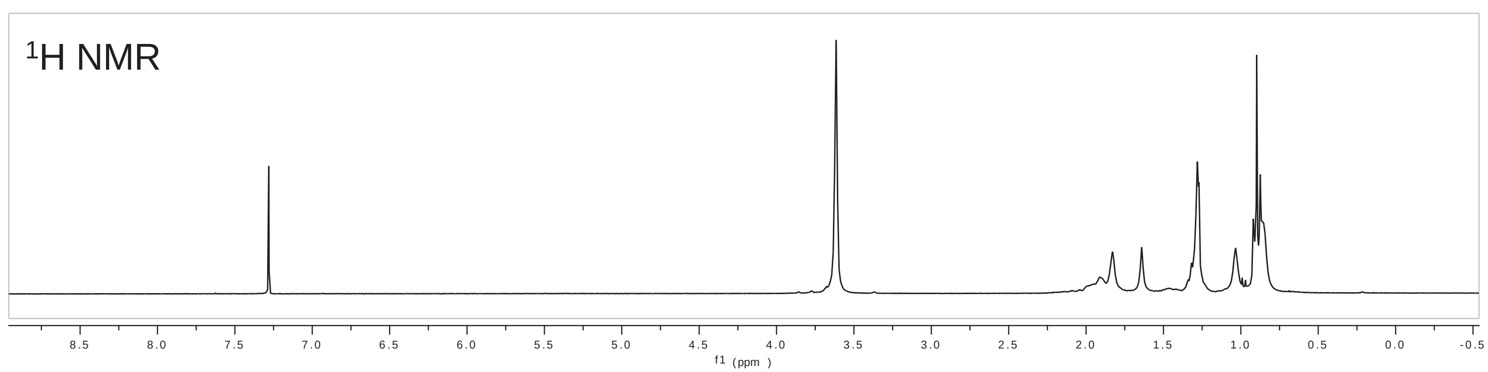
NMR Characterization of Copolymers



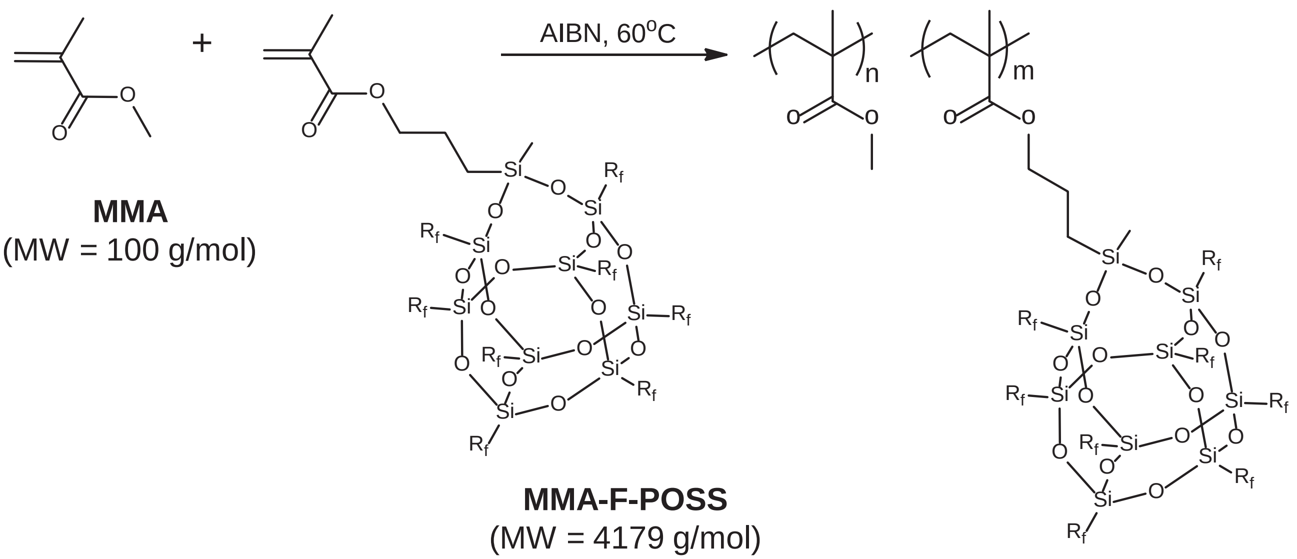








Initial Copolymerizations



Sample #	Weight (%)F-POSS	Mol Ratio (MMA:MMA-F-POSS)	Conversion (%)	Weight (%) FPOSS*	T_g (°c)	Solubility
1	6.3	655	42	2.74	165	PMMA solvents
2	21.6	145	71	14.4	165	PMMA solvents (takes time)
3	12.5	291				
4	25.0	125	62.5		126	PMMA solvents with small amount of AK-225G
5	50.0	42	92.5		127	THF-AK225G mixture (suspension)

Summary

- Structures were demonstrated to be reactive towards a variety of dichlorosilanes
- Solubility of F-POSS compounds were shown to be influenced by chemical functionality
- Functionality was shown to be influential on contact angle measurements
- F-POSS compounds have a near limitless potential in producing a variety of new hydrophobic, oleophobic, or ominiphobic polymer composites.
  - Reaction mechanisms, polymer composites, block copolymers, etc….